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Hybrid materials of pyrene substituted phthalocyanines with single-walled carbon nanotubes: structure and sensing properties

Esra Nur Kaya,^a Tamara Basova,^{bc} Maxim Polyakov,^b Mahmut Durmuş,^{*a} Burak Kadem^d and Aseel Hassan^d

Hybrid materials of single walled carbon nanotubes (SWCNT) were obtained by their non-covalent functionalization with asymmetrically polyoxyethylene substituted phthalocyanines (MPC-py (M = Cu, Co, 2H)) bearing one pyrene group as a substituent. The attachment of MPC-py molecules onto the SWCNT surface have been confirmed using Raman spectroscopy, SEM, TEM and thermogravimetric analysis. The pyrene substituents were introduced to the phthalocyanine macrocycle in order to improve π - π interaction between the MPC-py and SWCNT. The effect of the central metal on the formation and sensor properties of the MPC-py within the hybrids has been verified. It has been shown that the electrical response of the hybrid films to ammonia vapor in the concentration range of 10–50 ppm changes in the following order CuPc-py > CoPc-py > H2Pc-py, which was found to be in good correlation with the amount of phthalocyanine molecules adsorbed onto the SWCNT walls, as estimated by thermogravimetric analysis (TGA).

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Introduction

Hybrid materials based on carbon nanotubes (CNTs) have a great scientific interest due to their synergetic properties, which significantly enhance their technological application potentials. In order to modify CNTs various organic and inorganic compounds are applied. Metal nanoparticles, clusters, polymers, phthalocyanines, enzymes, hydrocarbons, and lipids were used as covalently and non-covalently adsorbed components on CNTs to form hybrids.^{1–3} Hybrids were confirmed to possess unique properties as compared to bare CNTs or modifier compounds.

In fact, hybrids have better solubility in comparison with bare CNTs which make them more attractive for different applications.^{4–7} Their films can therefore be deposited more easily by simple solution processing methods such as dip-dropping and spin coating methods. Hybrids have more advanced electrochemical properties and high sensitivity to various gases or liquids, faster response and relaxation times.^{8–11}

CNT hybrids have successfully been employed as sensors utilizing electrochemical, electric (ohmic), and optical detection

techniques,^{12–15} they have also been invariably examined as active layers element in solar cell^{16–18} and in magnetic devices.¹⁹ Ferrocene–CNT hybrid was proposed to apply for the detection of α -glutamate,²⁰ while CuPc-MWCNT was studied for the detection of organic compounds such as dimethyl methylphosphonate (DMMP).²¹ Another hybrid based on Si(OC₂H₅)₄–CNT system was studied as a gas sensor.¹⁰ This hybrid containing 1% CNTs was shown to possess the best response, allowing NO determination on the ppb level, but with less recovery. It was however shown that increasing CNT content leads to degradation of the sensor properties.

It is well-known that phthalocyanines have significant potential to be used as sensors of NH₃ and amines,^{22–24} NO_x,^{25–27} CO,^{28,29} H₂,^{30,31} H₂S and thiol³² vapours. Wang *et al.* have immobilized tetra-*tert*-butylphthalocyanine on carbon nanotubes by π - π interaction.³³

Pyrene was suggested to attach to CNTs strongly *via* π - π interaction.^{34–36} Torres *et al.* have used metal and metal-free pyrene substituted phthalocyanines to form stable electron donor-acceptor hybrids.³⁵ In our recent publication, we compared the structural features and sensor properties of hybrids of single walled carbon nanotubes (SWCNTs) with symmetrically polyoxyethylene octasubstituted ZnPc and similar asymmetrically substituted ZnPc-py with one pyrene group as a substituent.³⁷ It was shown that the interaction of ZnPc-py with SWCNTs is more favourable than in the case of ZnPc without pyrene. Comparing sensor response of bare SWCNTs with films of the SWCNT/ZnPc and SWCNT/ZnPc-py hybrids to NH₃ vapours, it was concluded that SWCNT/ZnPc-

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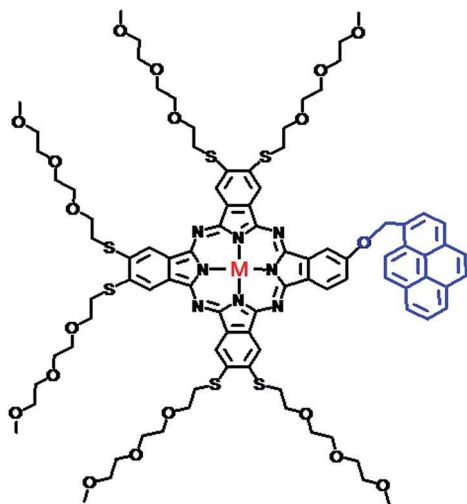


Fig. 1 General structure of AB3 type phthalocyanine compounds MPc-py, where M = 2H, Cu or Co.

py hybrid films have a larger response than that without the pyrene substituents.

In this work, we studied the hybrids of SWCNT with phthalocyanines bearing one pyrene and six polyoxyethylene substituents (MPc-py (M = 2H, Cu(II), Co(II)) (Fig. 1).

A comparative study of the structural features of the hybrid films and their sensor response to ammonia vapour (10–50 ppm) was carried out to verify the effect of central metal in phthalocyanine molecule.

Experimental

Materials

The methods of synthesis and purification of 4-nitrophthalonitrile,³⁸ 4,5-dichlorophthalonitrile,³⁹ 4-(1-pyrenylmethoxy) phthalonitrile,⁴⁰ 2,3,9,10,16,17-hexakis(4,7,10-trioxaundecan-1-sulfanyl)-23(24)-(1-pyrenyl methoxy) phthalocyaninato zinc(II) (ZnPc-py)⁴¹ have already been published elsewhere. All solvents used in the reactions were dried and purified as described by Perrin and Armarego.⁴² SWCNTs were purchased from Sigma-Aldrich and used without further purification or chemical treatment. The purity of the products was tested in each step using thin layer chromatography (TLC) (silica gel).

Equipment

The IR spectra in the range 650–4000 cm^{−1} were recorded by means of a Perkin Elmer Spectrum 100 FT-IR spectrometer with an attenuated total reflection accessory (ZnSe crystal). Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) measurements were carried out using a Bruker Daltonics microflex (Bremen, Germany) in dihydroxybenzoic acid matrix. A Varian 500 MHz spectrometer was used for registration of ¹H-NMR spectra in DMSO-d₆ solutions. Shimadzu UV-Vis-3101 and 2101 spectrometers were used for registration of the absorption spectra in the UV-visible region at room temperature. Thermogravimetric analysis

(TGA) was carried out using a Mettler Toledo Star^c Thermal Analysis System at a rate of 10 °C min^{−1} in a nitrogen flow (50 mL min^{−1}).

A Triplemate, SPEX spectrometer equipped with CCD detector was used for detection of Raman spectra in back-scattering geometry. An Ar-laser (488 nm, 40 mW) was used for the spectral excitation.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were obtained using a FEI-nova nanosem 200 and a JEM-2010 instrument at an accelerating voltage of 200 kV, respectively. The phthalocyanine films was prepared by evaporating a drop of hybrid dispersion in dichloromethane on a 200 mesh copper grid covered with a “holey” carbon film.

The films thickness was measured using spectroscopic ellipsometry (Woolam M2000VTM rotating analyser spectroscopic ellipsometer). DC-conductivity measurements were carried out using Keithley 236 semiconductors characterization system.

Synthesis

2,3,9,10,16,17-Hexakis(4,7,10-trioxaundecan-1-sulfanyl)-23(24)-(1-pyrenylmethoxy) phthalocyanine (H2Pc-py). Hexakis(4,7,10-trioxaundecan-1-sulfanyl)-23(24)-(1-pyrenylmethoxy) phthalocyaninato zinc(II) (ZnPc-py) (50 mg, 0.026 mmol)⁴¹ has been dissolved in pyridine (1 mL). An excess of pyridine hydrochloride salt (190 mg, 1.64 mmol) was added to the mixture and heated at 120 °C for 20 h. The reaction mixture was cooled to room temperature and poured into water. The resulted green product was precipitated and collected by filtration. In order to remove inorganic impurities this solid product was dissolved in dichloromethane, filtered and concentrated. The obtained crude product was purified on a silica gel column using dichloromethane : ethanol (25 : 1) mixture as an eluent; FT-IR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 3291 (N–H), 3053 (aromatic-CH), 2923–2855 (aliphatic-CH), 1597 (aromatic-C=N), 1245 (C–O–C), 1107 (–OCH₃); UV-Vis: (DMF, 1×10^{-5} M): λ_{max} nm (log ϵ): 728 (4.96), 699 (4.94), 666 (4.59), 634 (4.43), 345 (4.83); ¹H-NMR (500 MHz, DMSO-d₆) δ ppm: 8.72–7.87 (brd, 18H, Ar–H), 5.91 (s, 2H, OCH₂), 3.35–2.99 (brd, 90H, OCH₂, OCH₃), –5.98 (brd, 2H, NH); elemental analysis: calcd (%) for C₉₁H₁₁₂N₈O₁₉S₆: C 60.24, H 6.22, N 6.18; found: C 60.58, H 6.33, N 5.96; mass (MALDI-TOF), m/z (%): calcd. 1814.29, found 1814.0 [M]⁺.

2,3,9,10,16,17-Hexakis(4,7,10-trioxaundecan-1-sulfanyl)-23(24)-(1-pyrenylmethoxy) phthalocyaninato copper(II) (CuPc-py). A mixture of 2,3,9,10,16,17-hexakis(4,7,10-trioxaundecan-1-sulfanyl)-23(24)-(1-pyrenylmethoxy) phthalocyanine (H2Pc-py) (50 mg, 0.026 mmol) and copper(II) acetate dihydrate (10 mg, 0.055 mmol) were refluxed in dry *n*-pentanol (5 mL) for 24 h under argon atmosphere. The obtained crude product was purified on a silica gel column using dichloromethane : ethanol (25 : 1) solvent system as eluent. FT-IR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 3027 (aromatic-CH), 2922–2855 (aliphatic-CH), 1595 (aromatic-C=N), 1243 (C–O–C), 1086 (–OCH₃); UV-Vis: (DMF, 1×10^{-5} M): λ_{max} nm (log ϵ): 705 (4.92), 643 (4.40), 346 (4.63); elemental analysis: calcd (%) for C₉₁H₁₁₀N₈O₁₉S₆Cu: C 58.27, H 5.91, N 5.97; found: C 58.57, H 6.12, N 5.71; mass (MALDI-TOF), m/z (%): calcd. 1875.8, found 1876.5 [M + H]⁺.

2,3,9,10,16,17-Hexakis(4,7,10-trioxaundecan-1-sulfanyl)-23(24)-(1-pyrenylmethoxy) phthalocyaninato cobalt(II) (CoPc-py). A mixture of 2,3,9,10,16,17-hexakis(4,7,10-trioxaundecan-1-sulfanyl)-23(24)-(1-pyrenylmethoxy) phthalocyanine (H2Pc-py) (50 mg, 0.026 mmol) and cobalt(II) acetate tetrahydrate (10 mg, 0.040 mmol) were refluxed in dry *n*-pentanol (5 mL) for 24 h under argon atmosphere. The obtained crude product was purified on a silica gel column using dichloromethane : ethanol (25 : 1) solvent system as an eluent. FT-IR (ATR, $\nu_{\text{max}}/\text{cm}^{-1}$): 3043 (aromatic-CH), 2953–2853 (aliphatic-CH), 1597 (aromatic-C=N), 1235 (C–O–C), 1102 (–OCH₃); UV-Vis: (DMF, 1×10^{-5} M): λ_{max} nm (log ϵ): 690 (4.68), 625 (4.17), 332 (4.62); elemental analysis: calcd (%) for C₉₁H₁₁₀N₈O₁₉S₆Co: C 58.41, H 5.92, N 5.99; found: C 58.77, H 6.09, N 5.73; mass (MALDI-TOF), m/z (%): calcd. 1871.2, found 1872.4 $[\text{M} + \text{H}]^+$.

Preparation of SWCNT/MPC-py hybrids

MPC-py (5 mg) solutions were prepared by dissolving in 1 mL DMF and then sonicated for 15 minutes. Single walls carbon nanotubes were added in 3 mL DMF and then its suspension was subjected to sonication for 30 minutes. To obtain the hybrids SWCNT/MPC-py, the solution of MPC-py was dropped to the SWCNTs suspension. Addition of MPC-py solution have been continued until the green phthalocyanine solution is discoloured caused by adsorption of the phthalocyanine onto the SWCNT surface. After stirring for another hour the mixture was centrifuged, and the obtained precipitate was washed with DMF several times, centrifuged again and dried in vacuum.

Sensor properties study

The sensor response to low-concentration of NH₃ in the range 10–50 ppm was studied. Pure commercial NH₃ gas (“Dioksid”, Russia) was used as the NH₃ source. NH₃ was diluted by a syringe static volumetric method using nitrogen as the diluent gas. Diluted NH₃ was injected into the test chamber by a microsyringe. Pure nitrogen was injected to degas the test chamber after turning off the NH₃ gas. The relative humidity was about 50%RH.

SWCNT/MPC-py hybrids were obtained as thin films by spin coating their solutions in dichloromethane on the glass substrate with deposited interdigitated Pt electrodes (DropSens, G-IDEPT10). The dimension of gaps is 10 μm ; the number of digits is 125×2 with a digit length equal to 6760 μm ; cell constant is 0.0118 cm^{-1} . The electrical characterization of the hybrid films was carried out using a Keithley 236 electrometer by applying a constant dc voltage of 3 V.

Results and discussion

Synthesis and characterization of phthalocyanines

The studied metal-free phthalocyanine (H2Pc-py) was synthesized *via* demetaling of zinc(II) phthalocyanine derivative (ZnPc-py) using pyridine hydrochloride salt in pyridine.⁴³ Copper(II) (CuPc-py) and cobalt(II) (CoPc-py) phthalocyanine derivatives were synthesized by metaling of the metal-free phthalocyanine in *n*-pentanol using copper(II) acetate dihydrate and cobalt(II)

acetate tetrahydrate, respectively. The characterization of novel phthalocyanines (MPC-py) was achieved using matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF), fourier transform infrared (FT-IR), ultraviolet-visible (UV-Vis), proton nuclear magnetic resonance (¹H-NMR) as well as elemental analysis. The obtained results are consistent with the predicted structures as shown in Fig. 1.

The formation of metal-free phthalocyanine (H2Pc-py) from its zinc(II) counterpart (ZnPc-py) was identified by the appearance of N–H stretching peak at 3291 cm^{-1} in the FT-IR spectrum of this phthalocyanine.⁴⁴ This peak has disappeared after formation of Cu(II) and Co(II) phthalocyanines. For all synthesized phthalocyanine complexes (MPC-py), the vibration peaks were observed in the range $3053\text{--}3027 \text{ cm}^{-1}$ for the aromatic C–H stretching, $2953\text{--}2853 \text{ cm}^{-1}$ for the aliphatic C–H stretching, at 1597 cm^{-1} for the aromatic C=N stretching and in the range $1235\text{--}1245 \text{ cm}^{-1}$ for the Ar–O–Ar stretching.⁴⁴

The ¹H-NMR spectroscopy was only used for the characterization of the metal-free phthalocyanine (H2Pc-py) due to the paramagnetic behaviour of metal atoms (copper and cobalt) in the cavity for other phthalocyanines (CuPc-py and CoPc-py). In the ¹H-NMR spectrum, the main evidence for the formation of metal-free phthalocyanine (H2Pc-py) is the observation of NH protons in the phthalocyanine core at -5.98 ppm . These protons were observed at higher field due to magnetic anisotropy behaviour of phthalocyanine macrocycle. The aromatic protons for both phthalocyanine ring and pyrene group were observed between $8.72\text{--}7.87 \text{ ppm}$ as broad peak integrating 18 protons. The aliphatic protons on the methylene group of pyrene were observed at 5.92 ppm as a singlet peak. The other aliphatic protons on the polyoxy groups were observed between $3.35\text{--}2.99 \text{ ppm}$ as a broad peak integrating totally 90 protons.

In the mass spectra of studied phthalocyanines (MPC-py), the presence of molecular ion peaks at m/z 1814.0 $[\text{M}]^+$ for compound H2Pc-py, 1876.5 $[\text{M} + \text{H}]^+$ for compound CuPc-py and 1872.4 $[\text{M} + \text{H}]^+$ for compound CoPc-py confirmed the predicted structures of these phthalocyanines. The obtained elemental analysis data for all studied phthalocyanines (MPC-py) gave satisfactory results that were close to calculated values.

Characterization of SWCNT/MPC-py hybrids

Electronic absorption spectra. Electronic absorption spectra of SWCNT/MPC-py hybrid solutions in dimethylformamide (DMF) are compared to those of bare MPC-py solutions (Fig. 2). The spectrum of SWCNT is featureless as it was frequently reported in the literature.^{45,46} MPC-py exhibits typical electronic absorption spectra with two strong absorption regions, one in the wavelength range $620\text{--}730 \text{ nm}$ (Q-band) arising from the electron transitions from the highest occupied molecular orbital (HOMO) a_{1u} to the lowest unoccupied molecular orbital (LUMO) e_g and one in the range $320\text{--}400 \text{ nm}$ (B-band) which is attributed to the electron transitions from the (HOMO) a_{2u} to the (LUMO) e_g .⁴⁷ The most intensive peaks in the Q-band region can be ascribed to dominant monomer absorption at 690 nm for CoPc-py, 705 nm for CuPc-py, 728 and 699 nm for H2Pc-py while the shoulders with lower intensities at 625 , 643 , 666

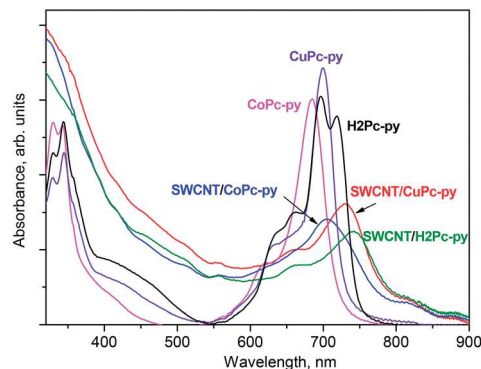


Fig. 2 UV-vis electronic absorption spectra of MPC-py and SWCNT/MPC-py hybrid solutions in DMF.

and 634 nm in the spectra of CoPc-py, CuPc-py and H2Pc-py, respectively, correspond to the molecular aggregation in DMF solution.

After hybridization of the phthalocyanines with SWCNTs, the obtained hybrids show different optical absorption spectra. The Q-bands in the absorption spectra of the SWCNT/MPC-py hybrids are broadened and their maxima are red-shifted in comparison with MPC-py spectra to 706, 730 and 742 nm for SWCNT/CoPc-py, SWCNT/CuPc-py and SWCNT/H2Pc-py, respectively. These changes are suggested to take place due to the π - π interaction between carbon nanotubes and phthalocyanine molecules, where phthalocyanines are usually considered as electron donors, while carbon nanotubes as acceptors.⁵

Raman spectra. Raman spectra of SWCNT/MPC-py hybrids are compared to those of pristine SWCNT in Fig. 3a. The ratio of intensities of the radial breathing modes (RBM), disorder (D) mode and graphite mode (G) are used to monitor functionalization with the phthalocyanines.^{48–52} The spectra were normalized to the graphite G-band at $\sim 1590\text{ cm}^{-1}$. The spectra of both SWCNT and SWCNT/MPC-py hybrids contain the typical disorder mode D at about 1340 cm^{-1} , and the G band at 1590 cm^{-1} . The inset of Fig. 3a is presented to show the enlarged section of the spectrum from 90 to 1300 cm^{-1} .

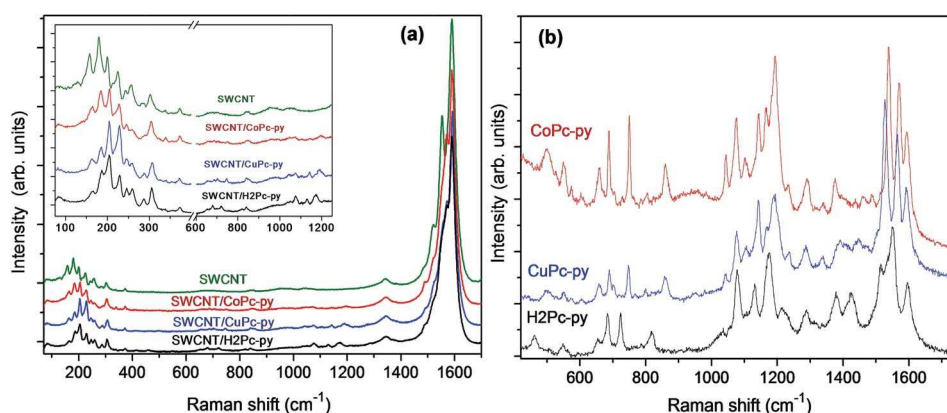


Fig. 3 (a) Raman spectra of pristine SWCNT and SWCNT/MPC-py hybrids in the range $90\text{--}1700\text{ cm}^{-1}$. The inset shows the same spectra in the range RBMs and phthalocyanine vibrations $90\text{--}1300\text{ cm}^{-1}$. (b) Raman spectra of MPC-py ($M = \text{Co}, \text{Cu}, 2\text{H}$).

Comparison of the SWCNT/MPC-py spectra with those of pure phthalocyanine derivatives (Fig. 3b) shows that the characteristic vibrations of phthalocyanine macrocycle are shifted noticeably due to interaction with SWCNT.

The intensity ratio of the D band to the G band (I_D/I_G) has a value of 0.053 in the spectrum of pure SWCNT, while the values of 0.059, 0.060 and 0.072 were obtained in the spectra of hybrids with H2Pc-py, CoPc-py and CuPc-py, respectively. This slight variation of the I_D/I_G ratio points to a non-covalent interaction of MPC-py derivatives with SWCNTs. The RBMs of SWCNT in the range $158\text{--}304\text{ cm}^{-1}$ (Fig. 3a) correspond to a distribution of SWCNT diameters in the range from 0.7 to 1.4 nm.^{53,54} Noticeable shifts in the RBM positions are observed in the range $158\text{--}225\text{ cm}^{-1}$. The RBMs at $158, 179, 200, 225\text{ cm}^{-1}$ of SWCNT are shifted to $164, 186, 205, 228\text{ cm}^{-1}$ after the adsorption of CuPc-py, to $162, 184, 204, 227\text{ cm}^{-1}$ after the adsorption of CoPc-py, and to $164, 186, 204, 228\text{ cm}^{-1}$ after the adsorption of H2Pc-py. The sensitivity of RBMs to the adsorption of polynuclear aromatic macrocycles by carbon nanotubes was demonstrated by Gotovac *et al.*⁵⁵ The π - π stacking interaction between carbon nanotube walls and the MPC core gives rise a shift to a higher frequency range due to the “hardening effect” described by Zhang *et al.*⁵⁶

Microscopy study. Adsorption of MPC-py to SWCNT walls can be further confirmed by examination of transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images. Fig. 4 shows TEM images of SWCNT/MPC-py hybrids; the coverage of phthalocyanines with the thickness of about

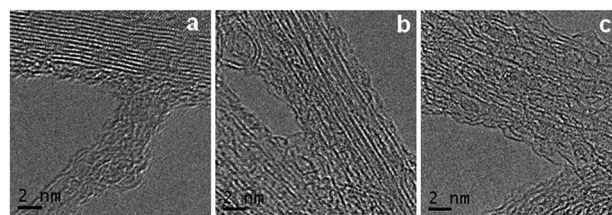


Fig. 4 TEM images of SWCNT/H2Pc-py (a), SWCNT/CuPc-py (b) and SWCNT/CoPc-py hybrids.

1.5–2 nm on the sidewall of SWCNT is clearly seen. D'Souza *et al.* visualized the attachment of alkylsubstituted porphyrins to SWCNTs by means of DFT calculations.⁵⁷ It has been shown that the MPc macrocycles have face-on arrangement with the alkyl chains surrounding the SWCNTs to some extent due to π - π and π -alkyl interaction.

Fig. 5 shows SEM images of the films of SWCNT/MPc-py hybrids deposited by spin coating. All hybrids demonstrate similar surface topography, which reveals that the SWCNTs based films are covered with MPc-py molecules. Smooth and homogeneous thin films of SWCNT/MPc-py hybrids can more easily be deposited because they have better solubility in comparison with bare SWCNT.

TG analysis. Fig. 6A shows the weight loss of about 4.3% in the case of pristine SWCNTs. It has also been revealed that the thermograms of compounds H2Pc-py (Fig. 6A), CuPc-py (Fig. 6B) and CoPc-py (Fig. 6C) present a loss of weight of 73.5%, 54.9% and 58.4%, respectively. A weight loss of 22.5%, 29.8%, and 25.4% for SWCNT/H2Pc-py, SWCNT/CuPc-py and SWCNT/CoPc-py, respectively was registered in the TGA experiment upon heating of SWCNT-MPc-py hybrids to 700 °C in the inert atmosphere. Taking into account the SWCNTs weight loss, the corrected weight loss due to MPc-py adsorption on the SWCNT surface was calculated to be 18.2%, 25.5% and 21.1% for H2Pc-py, CuPc-py and CoPc-py, respectively. Concerning the number of phthalocyanine molecules adsorbed on SWCNTs, a real ratios of 24.7% (18.2%/73.5%) for H2Pc-py, 46.4% (25.5%/54.9%) for CuPc-py and 36.1% (21.1%/58.4%) for CoPc-py have been estimated taking into consideration the weight loss of both MPc-py and SWCNTs. As a result, the number of carbon atoms per one H2Pc-py, CuPc-py and CoPc-py molecule was therefore estimated to be 460 $[(75.3\% \times 1814.29)/(24.7\% \times 12)]$, 180 $[(53.6\% \times 1875.8)/(46.4\% \times 12)]$ and 276 $[(63.9\% \times 1871.2)/(36.1\% \times 12)]$, respectively.

In our previous work³⁷ on zinc phthalocyanine derivative containing same pyrene group, the number of carbon atoms per one ZnPc-py molecule was estimated to be 336. The latter results have stimulated further work to prepare other metal-free and metallo phthalocyanine counterparts for comparison. SWCNT/CuPc-py has interacted almost 2 times more efficiently than the interaction within SWCNT/ZnPc-py. According to our calculations the best results were obtained for CuPc-py

derivative with the value of one CuPc-py molecule per 180 carbon atoms. As a result, the number of Pc molecules anchored on the SWCNT walls decreases in the following order: CuPc-py > CoPc-py > ZnPc-py > H2Pc-py.

Study of the sensor properties of SWCNT/MPc-py hybrids

Thin films of SWCNT/MPc-py in the thickness range 10–15 nm were spun onto interdigitated electrodes in order to investigate their sensing properties. Fig. 7 shows the normalized sensor response R ($R = (R - R_0)/R_0$; where R is the film resistance at the detected concentration of an analyte and R_0 is the baseline resistance) of SWCNT and SWCNT/MPc-py layers on exposure to 20, 30, 40 and 50 ppm of NH₃. The resistance of the SWCNT/MPc-py films increased as a result of adsorption of the electron donating NH₃ molecules, leading to charge transfer between the hybrid's film and NH₃ molecules. This result shows that the hybrids exhibit p-type behaviour.

Upon exposure to NH₃, all three SWCNT/MPc-py hybrids exhibited a more stable response compared to that of the SWCNT film.

For thin films of pure SWCNT it was difficult to achieve a stable and reproducible response because of difficulty to prepare smooth and homogeneous films on interdigitated electrodes. Combination of SWCNTs with phthalocyanine derivatives makes the hybrids more soluble in organic solvents that give the possibility to deposit highly conductive homogeneous films with large surface area. The SWCNT/hybrids therefore provide good prospect for sensor applications as has already been demonstrated in previous publications.^{21,22,37,58}

To analyse the role of the central metal in MPc molecules the response of three different SWCNT/MPc-py hybrid films towards NH₃ concentrations is depicted in Fig. 8. It can clearly be seen that the response value of the SWCNT/MPc-py hybrids towards ammonia decreases in the order CuPc-py > CoPc-py > H2Pc-py, which is in good correlation with the number of Pc molecules adsorbed onto the SWCNT wall, as estimated by TGA (Fig. 6). All three sensors demonstrate fast responses; the response time is about 5 s. The recovery time of CoPc-py and H2Pc-py sensors is 30 and 40 s, respectively, and it extends to 60 s in the case of CuPc-py film.

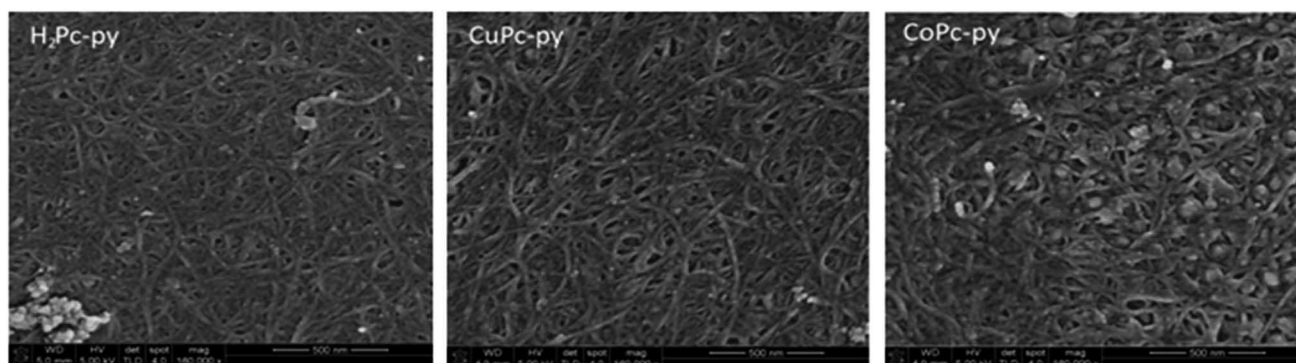


Fig. 5 SEM images of SWCNT/MPc-py hybrid films.

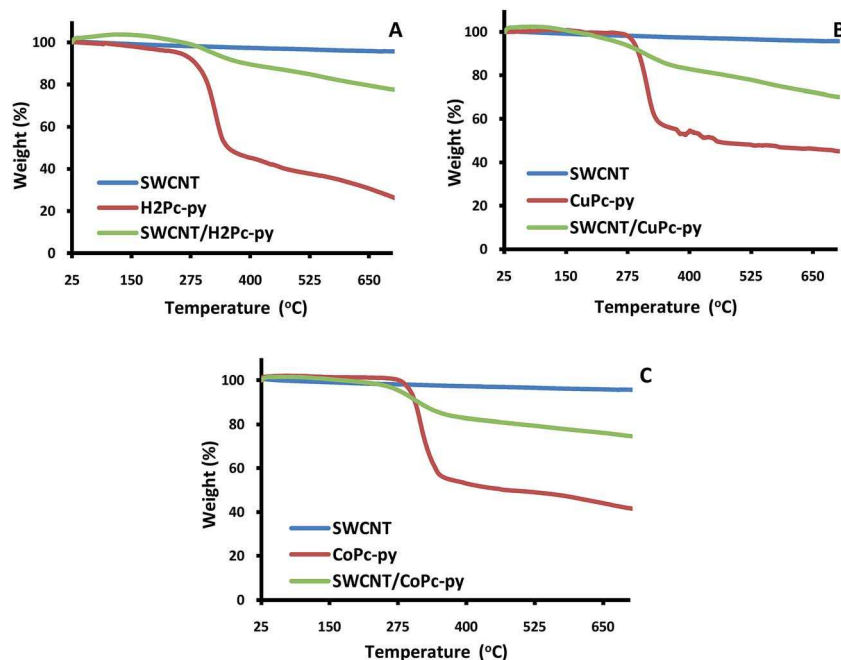


Fig. 6 Thermogravimetric analysis (TGA) of: (A) bare SWCNT, H2Pc-py and SWCNT/H2Pc-py hybrid; (B) bare SWCNT, CuPc-py and SWCNT/CuPc-py hybrid; (C) bare SWCNT, CoPc-py and SWCNT/CoPc-py hybrid.

These results demonstrate that the central metals in phthalocyanine molecules play important role in the determination of the sensor performance. The literature analysis shows that there are two main mechanisms of interaction of ammonia and amines with the phthalocyanines: van der Waals interaction and coordination *via* the central metal atoms.⁵⁹ It can also be inferred that the carbon nanotubes play the role of improving electron transport.⁶⁰ There have been numerous studies demonstrating the application of MPc and MPc hybrid materials with SWCNT as sensing elements for the detection of different gases, however studies concerning the influence of the

central metal in the phthalocyanine molecules has been sporadic.^{61–63} The effects of the central metal atom on gas sensor performance have been discussed for films of tetra-(*tert*-butyl)-5,10,15,20-tetraazaporphyrins (MTAP(*t*-Bu)₄, M = Pd, Ni, Co),⁶¹ 1,8,15,22-tetra-iso-pentyloxyphthalocyanine (MPc(iso-PeO)₄, M = Cu, Pb, Ni)⁶² and etioporphyrins of Cu, Zn, Ni, Co, Pt, Pd.⁶³ In these studies the change of the resistance upon interaction with NH₃ was measured. It was shown that the responses change in the following orders: PdTAP(*t*-Bu)₄ > NiTAP(*t*-Bu)₄ > CoTAP(*t*-Bu)₄ (ref. 61) and CuPc(iso-PeO)₄ > PbPc(iso-PeO)₄ > NiPc(iso-PeO)₄.⁶² This order in the sensor response has been clarified in

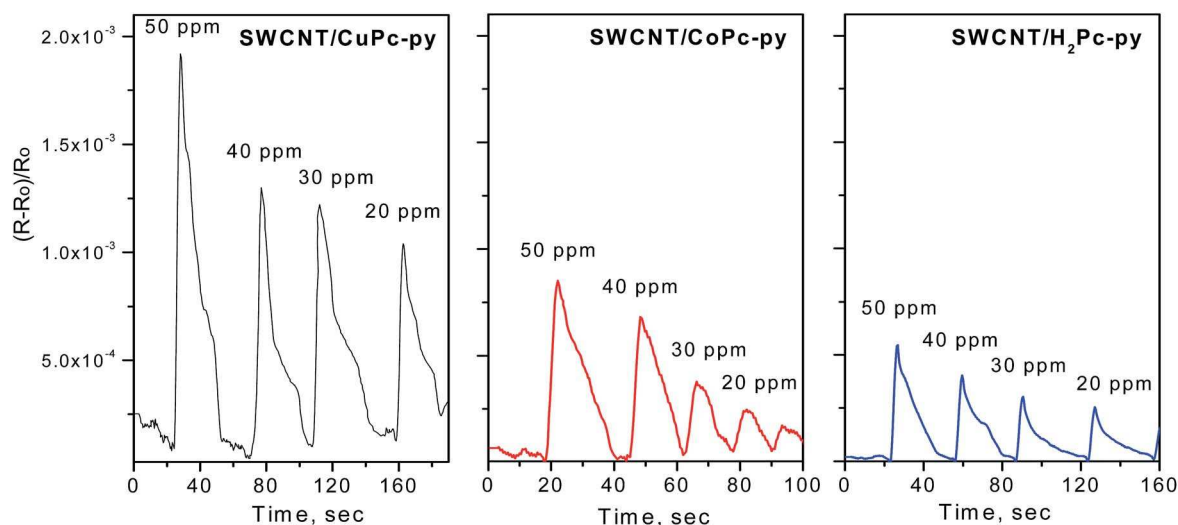


Fig. 7 Normalized sensor response of SWCNT/MPc-py hybrids to ammonia vapor at concentrations of 20–50 ppm.

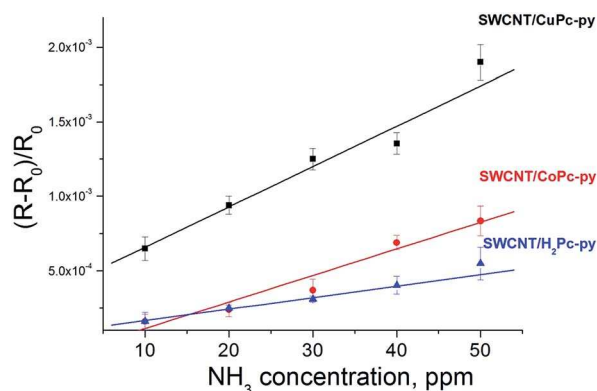


Fig. 8 Response of SWCNT/MPC-py hybrid films towards NH₃ concentrations.

terms of the central ion size: the larger ion radius, the more d-electrons. The d-electrons of central metal ion contribute to the π -electrons in the aromatic core and increases the donor power of porphyrin macro ring. Different order was however observed for metal etioporphyrins and as follows; CoEP > NiEP > CuEP > ZnEP.⁶³ The influence of the central metal in gas sensing properties in hybrids of MWCNT with 2,9,16,23-tetrakis(2,2,3,3-tetrafluoropropoxy) metal(II) phthalocyanine (TFPMPC, M = Co, Zn, Cu, Pb, Pd, Ni) was studied by Liang *et al.*⁶⁴ It was shown that the electrical response of TFPMPC/MWCNT hybrids to ammonia vapour decreases in the order of Co > Zn > Cu > Pb > Pd ~ Ni which was ascribed to the binding energies of MPC-NH₃ system calculated by DFT method. The electrical response order CuPc-py > CoPc-py > H₂Pc-py, obtained in this work is in good correlation with the number of Pc molecules anchored on the SWCNT surface, as estimated by TGA. Some discrepancies in the relation between the central metals and the sensor response to NH₃ vapours might be explained that the sensor response is determined not only by strength of interaction between the central metals of the molecules of active layer and analyte but also by many other factors *e.g.* substituents in the macro ring, number of active sites of the layer, sorption-desorption process and especially film thickness and morphology.

Conclusions

Hybrid materials of single walled carbon nanotubes were obtained by their non-covalent functionalization with asymmetrically polyoxyethylene substituted phthalocyanines MPC-py (M = Cu, Co, 2H) bearing one pyrene group as a substituent. The anchoring of MPC-py molecules onto the SWCNT surface has been confirmed by Raman spectroscopy, SEM and TEM microscopies and TGA.

It was shown that the amount of Pc molecules adsorbed onto the SWCNT walls decreases in the order CuPc-py > CoPc-py > H₂Pc-py. To verify the effect of central metal in the phthalocyanine molecule the electrical sensor response of SWCNTs/MPC-py hybrid films towards ammonia vapor (10–50 ppm) has been measured. The results show that the sensitivity of SWCNT/MPC-py films to NH₃ changes in the order CuPc-py > CoPc-py > H₂Pc-py,

which was found to be in good correlation with the amount of Pc molecules adsorbed onto the SWCNT walls, a result which was further evaluated by TGA measurements.

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